School of Physics and Astronomy

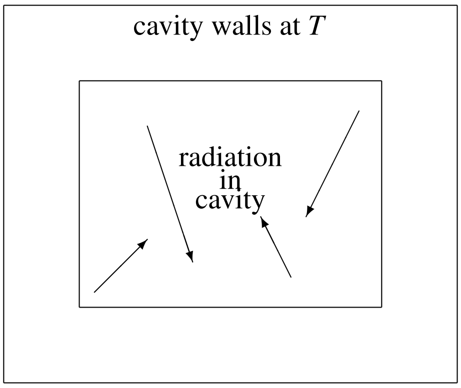
Junior Honours **Thermodynamics** GJA 2019-2020

Lecture TOPIC 12 (Finn 8.4 - 8.8)

Synopsis: Black Body Radiation and the birth of quantum mechanics

Thermal radiation as a thermodynamic system

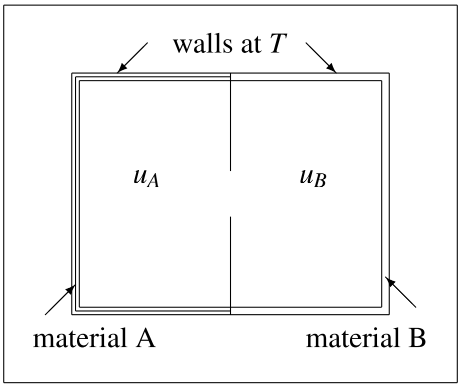
For radiation **inside** a cavity, the cavity walls at temperature T are considered to be the surroundings and the 'empty' cavity containing the radiation as the system. In equilibrium, the radiation inside the cavity is characterised by the temperature T of its surroundings. Its volume will be the volume V of the cavity. The radiation also has an energy (U), which increases with increasing temperature (think of a domestic electric oven). Reasoning based on thermodynamics and kinetic theory lead to a value for the pressure of the radiation.



Visualised as photons in a box, radiation in the cavity can be treated in an analogous way to molecules in a box: the kinetic theory. In particular the formula for pressure = $P = \frac{1}{3}Nmv_{rms}^2$ for N molecules **in unit volume** and root-mean-square velocity v_{rms} can be re-used, replacing v_{rms} with the speed of light c and using $E = mc^2$ to replace mass per unit volume (Nm) by its energy equivalent u/c^2 where u denotes energy per unit volume $u = U/V$. This gives an equation for the pressure exerted by the radiation, effectively the thermodynamic equation of state for radiation:

$$P = \frac{1}{3}u$$

Consider a partitioned oven having two joined compartments (A and B) made of different materials but both at the same temperature T. If $u_A > u_B$, the flow of radiation (heat) through the joining gap would make A cool and B heat up, without any work being done on the system by some external agency. A similar conclusion is reached for the case $u_B > u_A$. Thermal equilibrium requires equal energy density.



Furthermore, temperatures must be equal, so to avoid violating the Clausius version of the second law, u – summed over all wavelengths – has to be a function of temperature only: $u = u(T)$.

Now consider inserting filters in the gap connecting the two ovens. Now radiation at each wavelength can be seen as a separate system, so it can also be concluded that the energy density at a each and every wavelength is also a function of temperature only; $u_\lambda = u_\lambda(\lambda, T)$.

Equipartition and the ultraviolet catastrophe

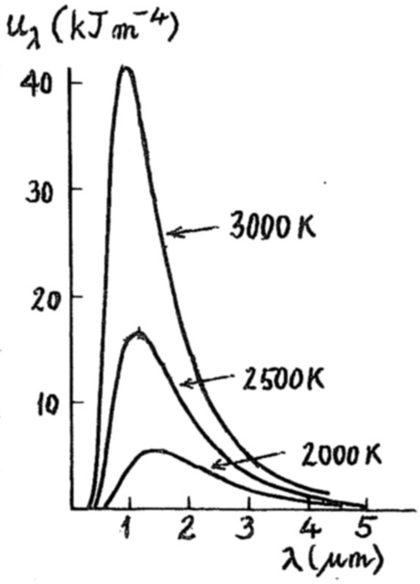
In classical mechanics, the equipartition theorem said that, in thermal equilibrium, energy is shared equally among all of its various forms, e.g. rotational, translational, vibrational motion.

For black body radiation, equipartition implied that energy should be shared equally between all frequencies. But since electromagnetism allows infinite possible frequencies, that would mean infinite energy.

Stefan's Constant, and the energy of cavity radiation

Classical thermodynamics allows deductions about cavity radiation, in particular resolving the so-called ultraviolet catastrophe.

It is observed that $u = \int_0^\infty u_\lambda d\lambda$ ("area under the curve") is very strongly **temperature**-dependent.



First consider the explicit dependence of u on T. From the central equation of thermodynamics, and one of the Maxwell's relations,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Using $P = \frac{1}{3}u$, $U = uV$ and $u = u(T)$ we get

$$u = \frac{1}{3}T\frac{du}{dT} - \frac{1}{3}u \implies 4\frac{dT}{T} = \frac{du}{u} \implies u = \left(\frac{4\sigma}{c}\right)T^4$$

We wrote the constant of integration as $4\sigma/c)$ to make a connection with Stefan's Law. It is shown below that the energy radiated per unit area of surface per second by an ideal radiator is equal to σT^4.

The full Planck distribution cannot quite be derived from Stefan's Law. However, we know it has a finite integral (no "ultraviolet catastrophe"), we know the T-dependence of that integral (Stefan's Law) and from experiment that when $u_\nu(\nu, T)$ plotted as a function of ν, it shows a single maximum, at a frequency that depends on temperature T.

Care is needed to distinguish energy density per unit wavelength u_λ from energy density per unit frequency u_ν when considering the Planck distribution. For example $\lambda = c/nu$ means $d\lambda = (-c/\nu^2)d\nu$.

Stefan's Law

We consider a perfect black body where all incident radiation is absorbed. Again, we apply kinetic theory to the photon gas, recalling that the number of particles striking unit area per second is $\frac{1}{4}n\bar{v}$ (proved below). Assuming the photons (speed c) have mean energy u/n (ie the energy density divided by the density), then the energy striking the area is $\frac{1}{4}cu$.

Substituting to u from above, and considering now that the radiation escapes through a small hole rather than being absorbed, we find that the radiation flux per unit area is.

$$e(T) = \frac{1}{4}cu = \sigma T^4$$

This is Stefan's Radiation Law, σ is a universal constant (Stefan's constant), $\sigma = 56.7nWm^{-2}K^{-4}$. Found empirically, thermodynamics reveals the fourth power results from living in a 3D universe, and σ emerges as a constant of integration.

Cavity walls - emissivity - Kirchoff's Law

Consider a small section of the wall of a cavity as the system. Consider this to be in equilibrium with radiation at temperature T. From the second law we must conclude that the energy radiated per unit surface over a small range of wavelengths $\varepsilon_\lambda(T)$ must be equal to that absorbed. Suppose that a fraction α_λ of the incident energy is absorbed, then:

$$\varepsilon_\lambda(T) = \frac{\alpha_\lambda c u_\lambda(\lambda, T)}{4}$$

This is Kirchoff's law relating emissivity to the absorption coefficient of a surface. Notice that $u_\lambda(\lambda, T)$ is a universal function. A more detailed derivation of this is given on p.5 of the notes online.

Radiation from a surface not in equilibrium

The above formula for the radiation from a surface was derived assuming thermal equilibrium between the wall and thermal radiation. However changing the radiation bathing the surface cannot change the emission which is determined only by the properties of the surface itself (notably its temperature). Therefore the surface continues to emit radiation at the same rate per unit surface (determined by $\alpha_\lambda(T)$ and T) even when not in equilibrium. This is the usual context in which the above radiation formula is used.

Other Thermodynamic quantities

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V = 4\sigma_o V T^3$$

with $\sigma_o = 4\sigma/c$, remembering that we've been using energy density, so total internal energy $U = uV$. Then, taking $S(T=0) = 0$, which we'll later see is the third Law,

$$S = \int \frac{C_v dT}{T} = \frac{4}{3}\sigma_o V T^3$$

and the enthalpy is:

$$H = U + PV = \frac{4}{3}\sigma_o V T^4 = TS$$

which we already knew was true for every frequency independently.

Now if we calculate the Gibbs Free Energy for black body radiation,

$$G = uV - TS + PV = \sigma_o V T^4 - \frac{4}{3}\sigma_o V T^4 + \frac{1}{3}\sigma_o V T^4 = 0$$

Which looks a bit weird. Microscopically, it means that the second law of thermodynamics allows a black body to spontaneously create or destroy photons without changing the Gibbs Free Energy: i.e. either process is allowed by the Second Law of Thermodynamics.

It is possible to reverse this whole chain of logic, starting with the observation that a black body to spontaneous creates and destroys photons, which requires $G = 0$, and thus $TS = H$ for photons.

Planck's Radiation Distribution Law: Uniqueness.

It is often claimed that Planck derived his Law from quantising the radiation. This is misleading, in fact he used thermodynamics, the derivation which requires postulating quantised energy came later.

Planck realised that the entropy was fundamental to the problem. From the Central equation we can relate the energy and entropy of the subset of photons with wavelength λ.

$$T_\lambda = \left(\frac{\partial u_\lambda}{\partial S_\lambda}\right)_V = T, \forall \lambda$$

we have defined an independent temperature of each subset T_λ. But because all the radiation is in thermal contact with all other wavelength, thermodynamics equilibrium demands that these temperatures are all equal and there is a universal relationship between the entropy and the energy.

This relationship must be the same function for each and every wavelength.

Notice that in this expression λ labels the thermodynamic system, it is *not* a state variable. You will sometimes see $u(\lambda,T)$, $u_\lambda(T)$ or $u_\lambda(\lambda,T)$. As derived above, in terms of thermodynamics, u is a function of T only.

Planck's Radiation Distribution Law: Functional Form

Everyone else was considering the relationship between energy, temperature and wavelength $u(\lambda,T)$. Planck now considered a quantity connecting energy and entropy, we'll call it $X = \left(\frac{\partial^2 s}{\partial u^2}\right)_V = \left(\frac{\partial(1/T)}{\partial u}\right)_V$

Although there was no theory for the full distribution, many things about $u(\lambda,T)$ could be measured. The total energy, the position of the peak and the energy dependence in tails of the distribution were well known. For large wavelengths Rayleigh showed that

$$u(\lambda,T) \propto T\lambda^{-4}; \qquad 1/T \propto \lambda^5/u \qquad X \propto u^{-2}$$

And for short wavelengths Wein had showed that

$$u(\lambda,T) \propto \lambda^{-5}\exp(-const/\lambda T); \qquad 1/T \propto \lambda \ln u\lambda^5 \qquad X \propto u^{-1}$$

Planck made a guess at a function which satisfied both limits $X = \frac{c_1}{u(u+c_2)}$ From here, he integrated wrt u to get the expression for $1/T$ in terms of u,

$$\frac{1}{T} = \int X du = \frac{c_1}{c_2} \ln \frac{u}{u+c_2}$$

reintroduced λ via constants of integration, and rearranged to get.

$$u_\lambda(T) \propto \lambda^{-5}\left(\frac{1}{e^{hc/\lambda k_B T} - 1}\right)$$

where Planck's "arbitrary constant" is written in its modern form hc/k_B

Planck's Law fitted both Rayleigh and Wein limits by construction, but also Stefan's Law and the observed maximum intensity.

Planck's Radiation Distribution Law: Meaning

To interpret the distribution, Planck still needed an expression for the entropy, and one which did not satisfy equipartition and gave lower entropy at higher ν. Noticing that the term in brackets is like the sum of an infinite geometric series (with r=$e^{-hc/\lambda k_B T}$), he turned (reluctantly) to Boltzmann's idea $S = k \ln W$, writing...

"If energy is considered to be a continuously divisible quantity, this distribution is possible in infinitely many ways. We consider, however - this is the most essential point of the whole calculation - Energy to be composed of a well-defined number of equal parts."

...and so quantum mechanics was born.

Radiation flux derivation

The flux of particles through a small orifice can be found by integrating the flux incident from the side of interest over all incident directions. Suppose the density of particles with velocity v is $n(v)$ is assumed isotropic, the fraction moving in a particular solid angle is just $d\Omega/4\pi$. Those incident at an angle θ to the normal to the surface in which the orifice is located and with velocity v arrive at rate per unit area $n(v)cos(\theta)$ at the orifice. The flux of particles with velocity v per unit area of the orifice is then given by:

$$\text{flux} = \text{particles sec}^{-1}\text{area}^{-1} = \int \frac{d\Omega}{4\pi} n(v)\ v\ cos(\theta)$$

$$\text{flux} = \int_{\theta=0}^{\theta=\pi/2} \int_{\phi=0}^{\phi=2\pi} \frac{d\phi d\theta sin(\theta)}{4\pi} n(v)\ v\ cos(\theta)$$

The integral over θ is easily done by substituting $x = cos(\theta)$ and noting that $dx = -sin(\theta)d\theta$ giving: flux $= \frac{1}{2}\int_1^0 -x\ n(v)\ v\ dx$

$$\boxed{(\text{flux with velocity }\ v) = \frac{1}{4} n(v)\ v}$$

This equation can be applied to a subset of photons with frequency between ν and $\nu + d\nu$; The total radiation flux is then obtained by integrating over all frequencies

$$(\text{Energy flux})_\lambda d\lambda = \frac{c}{4} u_\lambda d\lambda; \qquad \text{(i.e. the energy flux depends only on the energy density)}_\lambda$$

Considering two equal-temperature cavities as before connected by a filter. The Second law of thermodynamics tells us cannot have a net energy flow from one side to the other (no work is done) so that $\frac{c}{4} u_\lambda d\lambda$ and therefore u_λ (in a vacuum) must be a universal function and depend on temperature only (independent of cavity walls etc).